

# Demonstration of $\text{Mg}_2\text{FeH}_6$ as heat storage material at temperatures up to 550 °C

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Received: 30 September 2015 / Accepted: 29 October 2015 / Published online: 8 March 2016  
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**Abstract** The storage of heat at high temperatures, which can be used to generate electricity after sunset in concentrating solar power plants, is one of the most challenging technologies. The use of metal hydride could be one possibility to solve the problem. During the endothermic heat storage process, the metal hydride is decomposed releasing hydrogen, which then can be stored. During the exothermic reaction of the metal with the hydrogen gas, the stored heat is then released. Previous research had shown that Mg and Fe powders can be used at temperatures up to 550 °C for heat storage and shows excellent cycle stability over hundreds of cycles without any degradation. Here, we describe the results of testing of a tube storage tank that contained 211 g of Mg and Fe powders in 2:1 ratio. Twenty-three dehydrogenations (storage) and 23 hydrogenations (heat release) in the temperature range between of 395 and 515 °C and pressure range between 1.5 and 8.6 MPa were done. During the dehydrogenation, 0.41–0.42 kWh<sub>th</sub> kg<sup>−1</sup> of heat based on material 2 Mg/Fe can be stored in the tank. After testing, mainly  $\text{Mg}_2\text{FeH}_6$  was observed and small amounts of  $\text{MgH}_2$  and Fe metal can be detected in the hydride samples. This means that the heat storage capacity of the system could be further increased if only  $\text{Mg}_2\text{FeH}_6$  is produced during subsequent cycles.

## 1 Introduction

The storage of heat at high temperatures, which can be used to generate electricity after sunset in concentrating solar power plants, is one of the most challenging technologies [1]. While the currently most used technology of concentrating solar thermal power plants is parabolic trough systems (with working temperatures up to 400 °C, because of thermal stability of heat transfer oil used), the new generation of concentrated solar power plants is believed to be solar power towers. Here, the solar radiation is focused with flat, dual-axis tracking mirrors on a central receiver atop a collector tower, where the working fluid is heated to 600–1200 °C [2]. Molten salt mixtures are usually used as the working fluid for the storage of heat, utilising its heat capacity, which can be employed to store sensible heat before using it to boil water to drive steam turbines. Because of the relatively low sensible heat values, enormous amount of salt material becomes necessary for continuing electricity production in the night [3]. The storage capacities of the heat storage systems based on thermochemical reactions are several orders of magnitude higher than those based on molten salt. Examples of thermochemical heat storage systems currently under investigation are hydroxides, carbonates, metal oxides or metal hydrides [4]. Over the last years, it was shown that a temperature range from 300 to 1000 °C can be covered with metal hydrides depending on the type of the metal hydride compound [5–8]. A cycle stability over hundreds of heat storage and heat release processes is achievable making these materials an interesting solution for heat storage applications [9].

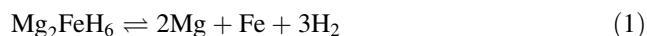
During the endothermic heat storage process, the metal hydride is decomposed releasing hydrogen, which then can be stored (e.g. in a gas pressure tank). During the

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exothermic reaction of the metal with the hydrogen gas, the stored heat is then released. Magnesium hydride was one of the first metal hydrides compounds explored for the use as thermochemical heat storage material. An amount of  $0.8 \text{ kWh}_{\text{th}} \text{ kg}^{-1}$  heat can be stored at temperatures around  $400^\circ\text{C}$  [9]. Unfortunately, the material is not useful for higher temperatures, because of sintering processes and a loss of heat storage capacity with increasing number of cycles [10]. More stable is a stoichiometric 2:1 mixture of both metallic magnesium and iron, producing dimagnesium iron hexahydride  $\text{Mg}_2\text{FeH}_6$  under hydrogen pressure (Eq. 1). The material can be used at temperatures up to  $550^\circ\text{C}$  for heat storage and shows excellent cycle stability over hundreds of cycles without any degradation [11, 12]. The gravimetric hydrogen content of  $\text{Mg}_2\text{FeH}_6$  is 5.5 wt%. Theoretically, it can store up to  $0.58 \text{ kWh}_{\text{th}} \text{ kg}^{-1}$  of heat, which is less than for  $\text{MgH}_2$ , but heat storage can be performed at much higher temperatures and lower pressure. Experimentally, a hydrogen storage capacity of around 5 wt% can be achieved, which results in a practical heat storage capacity of  $0.55 \text{ kWh}_{\text{th}} \text{ kg}^{-1}$ . Another advantage is the low price of the iron raw material.



Here, we present the first experimental and engineering results for the use of  $\text{Mg}_2\text{FeH}_6$  as a heat storage material for temperatures up to  $550^\circ\text{C}$  in two hundred-gram scale. This work is part of a larger development and demonstration project using  $\text{Mg}_2\text{FeH}_6$  as heat storage material and molten salt as heat transfer fluid. This prototype has been constructed for an overall amount of 5 kg  $\text{Mg}_2\text{FeH}_6$  useful for expected storage of  $2.7 \text{ kWh}_{\text{th}}$  heat at around  $500^\circ\text{C}$  and will be described in a future paper.

## 2 Experimental

Mg powder (Alfa Aesar, 325 mesh, 99 %) and Fe powder (Aldrich, >99 %) were used without further purification in 2:1 stoichiometric ratio. The two powders were mixed with a spatula and filled into the storage tank. The overall mass of the 2 Mg/Fe mixture was 211 g. Prior to the hydrogen absorption and desorption measurements, the filled tank was carefully evacuated at  $220^\circ\text{C}$  for 5 h and cooled down to room temperature under argon atmosphere, followed by another evacuation at  $480^\circ\text{C}$ . The 2 Mg/Fe mixture was then hydrogenated at this temperature at a hydrogen

pressure of 6.1 MPa for 70 min. After this initial hydrogenation step, the reactor was cooled down to room temperature and the hydride was dehydrogenated (heat storage) and hydrogenated (heat release) 23 times.

### 2.1 X-ray diffraction

The X-ray powder patterns for qualitative phase analysis were collected on a Stoe STADI P transmission diffractometer with a primary monochromator ( $\text{MoK}\alpha_1$ ) and a position-sensitive (Mythen 1K) detector. To prevent contact with air, all samples were filled into glass capillaries ( $\varnothing$  0.5 mm) in a glove box and sealed. The measured patterns were evaluated qualitatively by comparison with entries from the PDF-2 powder pattern database.

## 3 Results and discussion

### 3.1 Description of the heat storage tank system

The heat storage tank containing  $\text{Mg}_2\text{FeH}_6$  was manufactured from austenitic steel X6CrNiMoTi 17-12-2, suitable for high temperature and high hydrogen pressure conditions. The outer diameter of the reactor was 29 mm with a wall thickness of 2 mm and a tube length between the end caps of 400 mm. The inner volume and the outer volume of the reactor were 194.5 and 282.4 mL, respectively (without the volume of the thermocouple and the hydrogen supply). The overall mass of the storage tank without the 2 Mg/Fe mixture was 772 g. The individual masses of the different compounds including the 2 Mg/Fe mixture are listed in Table 1. The total mass of the filled tank was 983 g, resulting in 211 g of a stoichiometric 2 Mg/Fe mixture inside the storage tank. For the temperature measurement in the middle of the reactor tube length, a small, closed end capillary with a thermocouple (TC1, type K) was inserted at a 10 mm distance from the centerline of the tank (Fig. 1). The connection of the end caps, hydrogen supply tubes and the capillary for the thermocouple were all joined by laser welding.

Hydrogen distribution inside the tank system was achieved by a sintered metal tube with a length of 405 mm and diameter of 6 mm (0.5- $\mu\text{m}$  pore diameter) inserted in the middle of the tube reactor.

Heating was supplied by an electrical heating tape with an output power of 700 W. The heating tape was equipped

**Table 1** Masses of the tank components

$m_{\text{tube}}$ (g)	$m_{\text{SM}^*}$ (g)	$m_{\text{end caps}}$ (g)	$m_{\text{fitting}}$ (g)	$m_{\text{H}_2 \text{ supply}}$ (g)	$m_{\text{TC}^{**}}$ (g)	$m_{2\text{Mg}+\text{Fe}}$ (g)
536.3	90.7	41	38.6	38.8	26.3	211.1

\* Sintered metal, \*\* thermocouple

with a thermocouple (type K) and connected to a heating controller. On the outer wall of the tank, another thermocouple (TC2, type K) was installed at 35 mm distance from the welding of the hydrogen distribution tube (Fig. 1).

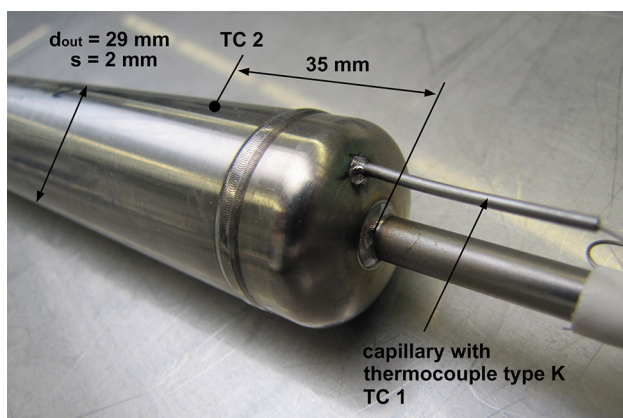
During hydrogenation, the heat was released to the environment. To avoid compaction of the powder mixture during the heat storage process, the tank was operated in a horizontal position. The temperature and pressure inside the tank system were monitored during these processes. De- and rehydrogenation measurements were taken either in a closed system (using three hydrogen reservoir cylinders of 3.785 L each) or in an open system where hydrogen was released through an exhaust pipe during dehydrogenation. For open system hydrogenations, the hydrogen was taken from a standard hydrogen cylinder. The

hydrogen storage capacity was calculated from the pressure differences inside the closed system during de- and rehydrogenation measurements. In the case of the open system, the hydrogen amount was measured with a mass flow controller (dehydrogenation) and mass flow meter (hydrogenation).

### 3.2 Heat storage and heat release experiments

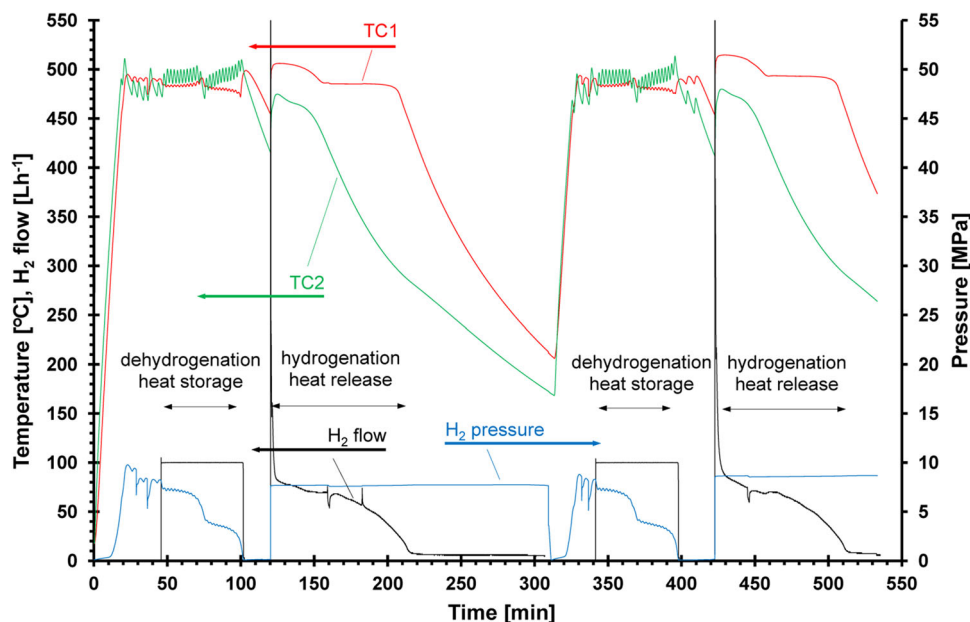
After the initial hydrogenation, the reactor was cooled down to room temperature and 23 dehydrogenations (heat storage) and 23 hydrogenations (heat release) in the temperature range between of 395–515 °C and pressure range between 1.5 and 8.6 MPa were performed. As typical examples, 10th and 11th dehydrogenation and 11th and 12th hydrogenation measurements are shown in Fig. 2 (open system). Temperature evolution inside the hydride bed (TC1) and at the outer wall of the storage tank (TC2) during the reaction time and the evolution of the hydrogen pressure and hydrogen flows inside the tank are displayed in Fig. 2. After the temperature in the hydride bed reached 495 °C, the pressure inside the tank was 9.7 MPa.

Dehydrogenation was started when the pressure reached 8.1 MPa. The mass flow controller was opened after 46 min, and the hydrogen flow was adjusted to 100 L h<sup>-1</sup>. Roughly 8.4 g of hydrogen was released in 55 min, corresponding to a hydrogen capacity of 3.8 wt%. The total heat,  $Q$ , was calculated according to Eq. 2, with  $M_{\text{H}_2} = 2.02 \text{ g mol}^{-1}$  for the molar mass of hydrogen and  $\Delta^R H$  for the heat of reaction.



**Fig. 1** Heat storage tank containing 211 g  $\text{Mg}_2\text{FeH}_6$

**Fig. 2** Two examples of performed dehydrogenations (heat storage) and two hydrogenations (heat release) during cycling tests with 211 g of  $\text{Mg}_2\text{FeH}_6$



$$Q = \frac{m_{H_2}}{M_{H_2}} \cdot \Delta^R H \quad (2)$$

The heat of reaction for hydrogenation and dehydrogenation of  $Mg_2FeH_6$  was found to be  $\Delta^R H = 77 \text{ kJ mol}^{-1} \text{ H}_2$  [12]. Since both  $Mg_2FeH_6$  and  $MgH_2$  phases are present during the reaction [13, 14], the  $\Delta^R H = 74 \text{ kJ mol}^{-1} \text{ H}_2$  for  $MgH_2$  [11] should also be taken into account for calculation. Since the exact phase composition was not known, the results are given in the range between a lower value using the heat of reaction for pure  $MgH_2$  and the upper value using the heat of reaction for pure  $Mg_2FeH_6$ . The theoretical gravimetric hydrogen capacity is 5.5 wt% if only  $Mg_2FeH_6$  is present [12]; however, if only  $MgH_2$  is formed, then the gravimetric hydrogen capacity can achieve a maximum 3.7 wt%.

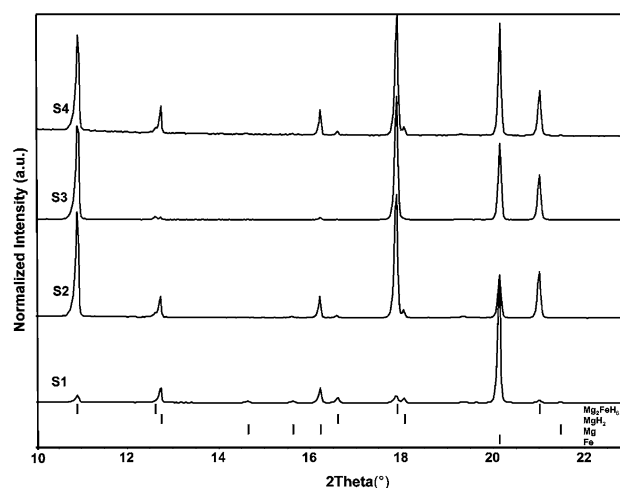
During the first dehydrogenation presented in Fig. 2, 308–320 kJ corresponding to  $0.41\text{--}0.42 \text{ kWh kg}^{-1}$  of heat had been stored in the tank.

The temperature fluctuations that are visible during the dehydrogenation measurement (green line, Fig. 2) are caused by the heat controller. The dehydrogenation was followed by a 20-min cooling down phase. When the temperature reached  $455^\circ\text{C}$ , the tank was pressurised to 7.7 MPa and the pressure was kept constant over the whole hydrogenation measurement time. After approximately 100 min, the  $\text{H}_2$  flow had dropped to nearly zero, concluding that the hydrogenation was complete. The temperature during hydrogenation stayed nearly constant at  $485^\circ\text{C}$ . When the hydrogenation was over, the temperature also started to drop (red line, Fig. 2). During the hydrogenation measurement, 8.5 g  $\text{H}_2$  was stored in the hydride bed, corresponding to a gravimetric capacity of 3.9 wt%. Using Eq. 2, it was calculated that a total amount of 312 kJ or  $0.41 \text{ kWh kg}^{-1}$  of heat was released during the hydrogenation step. In order to avoid the dehydrogenation of the formed hydride, the storage tank was left to cool down to approximately  $168^\circ\text{C}$ . After the first cycle (dehydrogenation and the subsequent hydrogenation process), a second cycle (dehydrogenation and hydrogenation) was carried out at the similar conditions. The time required for the hydrogenation process was approximately twice as long as for the dehydrogenation, which is explained by the characteristics of the material.

### 3.3 Characterisation of the heat storage material after cycling

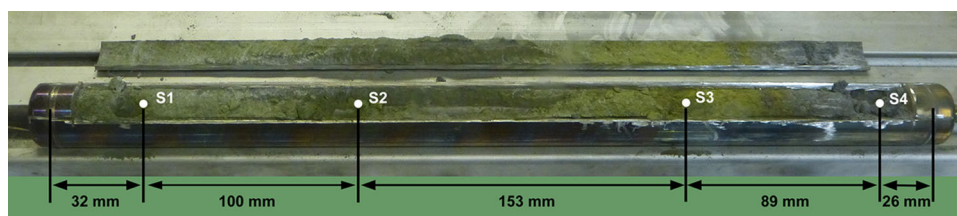
After the final hydrogenation measurement, the tank was opened inside an argon-filled glovebox (Fig. 3). A mixture of green- and grey-coloured material was observed along the opened tank (pure  $Mg_2FeH_6$  shows a deep green colour). Four samples (S1–S4) were taken from different positions (Fig. 4), and their phase composition was determined by XRD analysis.

The diffractograms of the samples S1–S4 are shown in Fig. 4. On the right side of the tank (Fig. 3), a complete grey-coloured material is observed (sample S1). This region corresponds to 1/6 of the overall tank length. Sample S1 consists mainly of sintered magnesium and iron. Only low diffraction intensities of  $MgH_2$  and  $Mg_2FeH_6$  phases could be detected. One possible reason for the sintering of the 2 Mg/Fe powder mixture could be an overheating of the tank tube on the right end during one of the dehydrogenation tests. During these tests, the temperature of the hydride bed in the middle of the tube achieved approximately  $570^\circ\text{C}$ , which is close to the melting point of Mg metal ( $650^\circ\text{C}$ ). Rehydrogenation of this sintered material seems to be not possible under the experimental conditions. The sintered material reduces the overall heat



**Fig. 4** X-ray powder diffraction patterns of samples S1–S4 after the final hydrogenation test

**Fig. 3** Open heat storage tank for the determination of the phase composition after the final hydrogenation. The points marked the positions of the samples S1–S4 taken for X-ray diffraction analysis





storage/hydrogen storage capacity of the tank. However, the remaining part of the tank shows powder with the dark green colour of  $\text{Mg}_2\text{FeH}_6$ . At the positions of sample S2 and sample S3, the highest diffraction intensities for  $\text{Mg}_2\text{FeH}_6$  are detected. While in sample S2, small amounts of  $\text{MgH}_2$  are present, this is not the case in sample S3. At the position of sample S4, mainly  $\text{Mg}_2\text{FeH}_6$  and  $\text{MgH}_2$  are found together with Mg metal. This part of the reactor shows also a dark green colour. In all 4 samples, the diffraction pattern of residual Fe metal is observed.

## 4 Conclusion and outlook

Heat storage at temperatures of 500 °C was demonstrated with the reversible  $\text{Mg}_2\text{FeH}_6$  hydride system on a 200-g material level. A hydrogen capacity of 3.8 wt% was observed during the de- and rehydrogenation experiments. For a complete conversion of the 2 Mg/Fe mixture into  $\text{Mg}_2\text{FeH}_6$ , a theoretical heat amount of  $0.58 \text{ kWh}_{\text{th}} \text{ kg}^{-1}$  can be expected. The calculated heat amount based on the hydrogen storage capacity of the material 2 Mg/Fe is between 0.41 and  $0.42 \text{ kWh}_{\text{th}} \text{ kg}^{-1}$ . Considering that 1/6 of the material inside the storage tank was sintered and could not be used for heat storage, the storable heat of the remaining material increased up to  $0.51 \text{ kWh}_{\text{th}} \text{ kg}^{-1}$ . This value corresponds to the storable heat amount described in former publications. After 23 cycles, the remaining  $\text{MgH}_2$  or Fe metal can be detected in hydride samples taken from different positions in the storage tank. That means that the storage capacity of the system could be increased with further de- and rehydrogenation processes.

Presently, a scaled up system with 5 kg of heat storage material (2 Mg/Fe) is under construction. The expected storable heat amount of the system is  $2.7 \text{ kWh}_{\text{th}}$ . Heat transfer at 500 °C will be accomplished with a molten salt mixture, which is often used as a heat transfer fluid in solar thermal power plants.

**Acknowledgments** In addition to the basic funds of the Max-Planck-Society, this project (No. 17850N) of the research association

IUTA has been supported by AiF as part of the industrial cooperative research and development (IGF) programme by the German Federal Ministry of Economic Affairs and Energy (BMWi) on the basis of a decision of the German Federal Parliament. XRD analysis was performed by Dr. Claudia Weidenthaler from the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr, Germany. Her support is gratefully acknowledged.

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